

ACQUISITION OF REGIONAL AIR QUALITY
MODEL VALIDATION DATA FOR NITRATE, SULFATE,
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ABSTRACT

An intensive field study was conducted throughout California's South Coast Air Basin to acquire air quality model validation data for use with aerosol nitrate formation models. Aerosol nitrate, sulfate, ammonium, other major ionic aerosol species, nitric acid gas and ammonia were measured concurrently at ten sites for forty-eight consecutive hours during the period August 30-31, 1982. Ozone, NO and NO_x were measured at all locations, and PAN was measured at Pasadena and Riverside, completing a nitrogen balance on the air masses studied.

The product of the measured nitric acid and ammonia concentrations ranged from less than 1 ppbv² to greater than 300 ppbv² during the experiment, providing a wide range of conditions over which comparisons can be drawn between chemical equilibrium calculations and experimental results. The ionic material in the aerosol phase was chemically more complex than is assumed by present theoretical models for the equilibrium between NH₃, HNO₃ and the aerosol phase, and included significant amounts of Na⁺, Ca⁺⁺, Mg⁺⁺, K⁺ and Cl⁻ in addition to NH₄⁺, SO₄ and NO₃⁻. Results of the experiment showed that aerosol nitrate levels in excess of 20 µg m⁻³ accumulated in near-coastal locations in the morning of August 31, followed by subsequent transport across the air basin. Trajectory analysis showed that the afternoon aerosol nitrate peak observed inland at Rubidoux near Riverside was associated with the same air mass that contained the high morning nitrate levels near the coast, indicating that description of both transport and atmospheric chemical reactions is important in understanding regional nitrate dynamics.

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1.0 Introduction

Ammonia and nitric acid vapor react to form ammonium nitrate aerosol. This is important because ammonium nitrate containing aerosols account for a significant fraction of local and regional visibility problems, particularly in Los Angeles and Denver (White and Roberts, 1977; Cass, 1979; Groblicki et al., 1981). Nitric acid concentrations also are important because of their contribution to wet and dry acid deposition processes. Since NH_4NO_3 formation acts as an important sink for nitric acid, the formation of NH_4NO_3 must be understood if nitric acid levels are to be controlled in a deliberate fashion. Reliable air quality models are needed if emission control strategy development is to proceed. But before air quality models that compute aerosol nitrate and nitric acid concentrations are used for emission control strategy testing, the accuracy of their predictions must be evaluated.

An air quality model for NH_4NO_3 formation and transport recently has been developed (Russell et al., 1983). The Caltech photochemical airshed model developed by McRae and Seinfeld (1983) is used to compute gaseous HNO_3 concentrations from reactive hydrocarbon and oxides of nitrogen emissions. An inventory of ammonia emissions is introduced into the model. Then NH_4NO_3 concentrations are computed at thermodynamic equilibrium between gaseous HNO_3 and NH_3 using the approach outlined by Stelson and Seinfeld (1982a,b).

To date, this model has been tested in its trajectory form against the time series of gaseous ammonia, particulate ammonium ion and particulate nitrate ion concentration measurements at El Monte, California on a summer day during 1974. Although the model appears to perform well, the ability to confirm this conclusion is limited by the absence of field data on gaseous nitric acid during that event, and by the potential for artifact nitrate formation during sample collection by the measurement methods used in 1974. Better model validation data are needed.

Ideally, an air quality model validation data set for aerosol nitrate formation should provide measurements of all relevant gaseous species: NO , NO_2 , HNO_3 , NH_3 , PAN (and O_3 if photochemical oxidant concentrations are to be checked as well). In addition, the concentration of the aerosol species NO_3^- , $\text{SO}_4^{=}$, NH_4^+ should be measured along with all other ionic species that are present in the aerosol. Temperature and relative humidity data are needed to compute the equilibrium dissociation constant that relates gaseous HNO_3 and NH_3 to the aerosol phase. Simultaneous measurements at a number of widely spaced monitoring sites are desirable if an Eulerian grid-based version of the aerosol nitrate formation model is to be tested. Two or more consecutive days of observation are required in Los Angeles if air is to be tracked from the marine environment all of the way to the eastern end of the air basin near Riverside. Low artifact measurement methods are desired.

The purpose of this paper is to report on the acquisition of such an aerosol nitrate air quality model verification data set in southern California.

2.0 Experimental

A field experiment was conducted in the South Coast Air Basin (SCAB) that surrounds Los Angeles during the period August 30-31, 1982. Moderate levels of photochemical smog were encountered during the two days studied. Both days were warm with scattered clouds. Peak temperatures reached 35° and 37°C on August 30 and 31 respectively at the eastern end of the Los Angeles basin. During the afternoons, onshore winds transported pollutants inland, with typical wind speeds of about 5 m sec⁻¹. This combination of high temperatures and inland transport resulted in a peak 1-hr average ozone concentration of 0.18 ppm on August 30, increasing to a 1-hr average peak ozone level of 0.26 ppm in the Riverside area on August 31.

Ten monitoring sites were established at the locations shown in Figure 1. The sampling network operated for 48 consecutive hours from midnight at the start of the first day to midnight at the end of August 31. Two-hour average and four-hour average measurements of $\text{HNO}_3(\text{g})$, $\text{NH}_3(\text{g})$, NO_3^- , NH_4^+ , $\text{SO}_4^{=}$ and other major ionic species were obtained at each site. All sites except Riverside were co-located with a South Coast Air Quality Management District (SCAQMD) or California Air Resources Board (CARB) continuous air monitoring station, and hourly average data on NO , NO_2 , O_3 and SO_2 were obtained by cooperation

with these agencies. Site descriptions are given by the U.S. Environmental Protection Agency (1973, 1978 et seq.). PAN was measured by electron capture gas chromatography, and NO and NO₂ were measured by chemiluminescence by researchers at the University of California at Riverside (UCR). PAN also was measured by the same principle at Caltech in Pasadena.

The aerosol, nitric acid and ammonia sampling apparatus for this experiment is shown schematically in Figure 2. Aerosol nitrate and nitric acid concentrations were measured both by dual filter methods and by the denuder difference method. Gaseous ammonia was measured by a dual filter method using oxalic acid impregnated filters as a sink for NH₃. Filter holders were of open-faced design so that any large particle nitrates would be collected. The sampling apparatus was surrounded by a bug screen and shaded by a sun shield to prevent nitrate volatilization through over-heating. Nine of the ten sampling sites shown in Figure 1 were equipped as indicated in Figure 2, while the 10th site at Riverside (UCR) consisted of only the two sampling lines that contained dual filter packs.

In the dual filter method for nitric acid determination, air was drawn at a rate of 10 lpm through a dual filter pack (Grosjean, 1983; Spicer et al., 1982; Appel et al., 1980). A teflon prefilter (Membrana, Zefluor, 47 mm diameter, 1 μm pore size) first removed the aerosol phase constituents. Gaseous nitric acid that passed through the inert teflon prefilter was collected as nitrate on a nylon after-filter (Ghia Corp., Nylasorb, 47 mm diameter, 1 μm pore size).

Filters, after exposure, were sealed immediately in petri dishes and chilled until analysis to minimize volatilization from the samples.

Water soluble material was extracted from these filters by mechanical shaking in distilled-deionized-distilled water for 1 hour or more. Measured extraction efficiencies typically were above 97%. The extract was divided for subsequent chemical analysis. The aerosol material extracted from the teflon prefilters was analyzed for nitrate, sulfate, chloride, potassium and sodium ion using Dionex Model 10 and Model 2120 ion chromatographs (Mueller et al., 1978). Divalent cations (calcium and magnesium) were measured using a Varian Techtron model AA-6 atomic absorption spectrophotometer (Varian, 1975). Ammonium ion on the teflon filters was determined by the phenol-hypochlorite method (Salorzano, 1967). Nitric acid concentrations were determined by extracting the nitrate ion collected on the nylon after-filters, with chemical analysis by ion chromatography as described above. Analytical uncertainties were assessed by analysis of reagent grade standards prepared in the range 0 to 5 ppm(wt/vol aqueous solution). Five replicate analyses of each of three standard solutions that span the concentration range of interest for each species were used to estimate the uncertainty associated with the laboratory procedures. The relative uncertainty associated with these measurements is shown in the first data column of Table 1. A contribution due to the variability of the filter blanks was added to this analytical error. More than twenty blank filters of each type were taken into the field but not exposed. The average blank values from these filters were subtracted from the

measured filter loadings. The contribution to the uncertainty in these measurements due to the variability of the filter blank also is shown in Table 1. This uncertainty in the filter blank governs the lowest quantifiable pollutant concentrations during this experiment. A complete listing of the data from this experiment and their associated uncertainties has been compiled (Russell and Cass, 1983).

The dual filter method for measuring aerosol nitrate and nitric acid has the advantage of simplicity, low cost, sensitivity and ability to produce both particulate and gaseous nitrate concentration data from the same air stream. Results from the nitric acid measurement method intercomparison (Spicer et al., 1982) conducted in the SCAB showed that the dual filter measurements were highly correlated with the median value obtained by all competitive nitric acid measurement methods. One of the two groups of investigators that used a teflon-nylon filter pair during the intercomparison study obtained results suggesting a small positive proportional bias, while a second group obtained results that suggest no significant bias when measuring nitric acid. Dual filter methods are susceptible to both positive and negative errors. Volatilization of ammonium nitrate would decrease measured nitrate aerosol (Appel et al., 1980). Nitric acid may also react with collected aerosol increasing the measured nitrate aerosol (Appel et al., 1980; Spicer and Schumacher, 1979).

The second method used for nitric acid determination during the present experiment was based on the diffusion denuder design described by Forrest et al. (1982), except that 10 sodium carbonate coated tubes

30 cm in length were contained within each denuder housing. At a total air flow rate of 4.9 lpm, laminar flow was achieved inside the denuder tubes at a nominal Reynolds number of 175 based on tube diameter. Air flowing through the denuder was stripped of nitric acid by reaction with the tube walls. Particulate nitrate (PN) penetrated the denuder and was collected on the nylon after-filter. A separate parallel sample line operating at 4.9 lpm contained a single nylon filter used to collect total inorganic nitrate (i.e. nitric acid plus aerosol nitrate). Nitric acid concentrations by the denuder difference method were obtained by subtracting the particulate nitrate concentration from the total inorganic nitrate concentration. Nitrate ion levels on these nylon filters were determined by water extraction and ion chromatography, with filter blank subtraction as described previously.

Nitrate measurements obtained by denuder also are susceptible to interferences. Large particle nitrate may be lost in the denuder by impaction. Laboratory experiments performed on the denuders used in this experiment show losses of about 30% for particles larger than 4 μm in diameter (Strand, 1983). Because of this measurable bias in the denuder system, nitric acid concentrations presented in this paper will be based on the dual filter method.

Gaseous ammonia concentrations were determined from the dual filter pack shown in Figure 2 that contained an oxalic acid impregnated back-up filter. The aerosol phase containing ammonium ion first was removed by a teflon prefilter (Membrana, Zefluor, 47 mm diameter, 1.0 μm pore size). Ammonia gas remaining in the air stream was collected

by reaction with an oxalic acid impregnated glass fiber filter (Gelman Type AE, 47 mm diameter) (Yoong, 1981; Appel et al., 1980; Cadle et al., 1980). After collection, filters were sealed and chilled as described previously. Ammonia concentrations were determined from the ammonium ion collected on the oxalic acid impregnated filters by a modified version of the phenol-hypochlorite method (Salorzano, 1967). The excess oxalate and acid on the glass fiber filters interfered significantly with the method of Salorzano (1967), so the method was modified, adding a phosphate buffer (Harwood and Kuhn, 1970) and additional hydroxide. The modified method is described by Russell (1983) and was found to give reproducible results with a correlation coefficient of $r = 0.99$. Standard deviations for recovery of NH_4^+ standards containing 1 ppm and 0.5 ppm (N by wt) were 2.5% and 3.5% respectively.

The calculated equilibrium dissociation constant for the $\text{HNO}_3\text{-NH}_3\text{-NH}_4\text{NO}_3$ system is highly dependent on ambient temperature and relative humidity. Temperature measurements to accompany each ambient sample were obtained from nearby weather monitoring stations, where possible, or from temperature measurements that were taken at the air monitoring site by the station operators using mercury thermometers. Instantaneous temperatures were taken each hour. Relative humidities were computed from measured dew point saturation temperatures that are monitored at a number of locations in the SCAB. Dew point temperatures were interpolated to the location of each monitoring site by the method of Goodin et al. (1979).

3.0 Results

Based on previous descriptions of aerosol nitrate concentrations in the Los Angeles area (Appel et al., 1978), high aerosol nitrate concentrations were expected in the Riverside area in the late afternoon due to production of nitric acid in the plume downwind of metropolitan Los Angeles. High aerosol nitrate levels (above $25 \mu\text{g m}^{-3}$) were observed at Rubidoux as expected, as is seen in Figure 3a. However, unexpectedly high nitrate levels also were observed at near-coastal sites like Lennox and Long Beach in the morning of August 31, as seen in Figure 3c.

Hourly averaged data on surface wind speed and direction at 39 monitoring sites in Southern California were acquired from governmental agencies for the period August 30-31, 1982. A mass-consistent wind field defined over a 5 km by 5 km grid system that covers the geographic area shown in Figure 1 was developed for each hour by the method of Goodin et al. (1979). Air parcel trajectories were integrated over these grided wind fields using 10 minute time steps. Trajectory analysis shows that the peak nitrate concentration at Rubidoux on the afternoon of August 31 is related to the coastal peak observed at Long Beach earlier that morning. A forward trajectory drawn from the nitrate peak in the Long Beach area at 1100 hours on the morning of August 31 passes within 3.5 km of Rubidoux between 1700 and 1800 hours in the late afternoon at the time of the nitrate peak in the eastern portion of the air basin (see Figure 3b). A backward trajectory drawn from Long Beach at 1100 hours on August 31 shows that

that air mass first crossed the coastline during the sea breeze portion of the late afternoon of August 30. At night, wind speeds dropped to less than 0.5 m sec^{-1} with variable wind direction. The air mass stagnated overnight in the Long Beach, an area of high NO_x emissions (see Figure 6 in Russell et al., 1983). The high nitrate concentration observed at Long Beach in the morning of August 31 resulted from progressive aerosol accumulation within a largely stagnant and stable air mass. This nitrate-rich air parcel then was advected inland on the next day's sea breeze. It appears that transport may play as important a role as chemical reaction in accumulating high nitrate levels.

A balance on the ionic material in the samples taken at Long Beach is shown in Figure 4. The major constituents are NH_4^+ , NO_3^- , and $\text{SO}_4^{=}$, but Na^+ , and Ca^{++} often account for about one third of the cations present, suggesting sea salt and soil dust contributions to the aerosol samples. Na^+ usually is present in excess of Cl^- , suggesting that reaction with strong acids like H_2SO_4 or HNO_3 has displaced some of the chloride from the sea salt portion of the aerosol (Martens et al., 1973; Duce, 1969; Robbins et al., 1959; Hitchcock et al., 1980). The ion balance closes closely in spite of the fact that $\text{CO}_3^{=}$, OH^- and H^+ concentrations were not measured. Previous studies in the SCAB show the presence of very low carbonate carbon levels in the aerosol (Mueller et al., 1972). Large amounts of hydrogen ion would not be expected because of the great excess of ammonia present during this experiment.

The composition of the aerosol observed inland at Riverside is shown in Figure 5. The largest contributors to the ionic material are NH_4^+ and NO_3^- , but noticeable amounts of K^+ , Mg^{++} , Ca^{++} , Na^+ and Cl^- also are found. Note that Cl^- arrives with the aerosol between 1600 and 1800 hours on August 31 near the time of arrival of the trajectory from Long Beach discussed previously. The important point to note from these ion balances is that the ionic material in the actual aerosol is much more complex than the mixed sulfate, nitrate and ammonium salts that can be described by present theoretical models for the equilibrium between NH_3 , HNO_3 and the aerosol phase.

Gas phase HNO_3 concentrations are compared to aerosol NO_3^- at the polluted near-coastal sites at Long Beach and Lennox in Figure 6. Nearly all of the inorganic nitrate is in the aerosol phase. In contrast, Figure 7 shows that ammonia is partitioned about equally between $\text{NH}_3(\text{g})$ and aerosol NH_4^+ at Long Beach, while at Lennox ammonia gas concentrations often were quite elevated, suggesting an NH_3 source upwind of Lennox (possibly at a nearby refinery or at the nearby Hyperion sewage treatment plant).

Inland from the coast, gaseous nitric acid concentrations begin to increase in the late morning and early afternoon, due possibly to photochemical production of HNO_3 or to volatilization of NH_4NO_3 . This can be seen in Figure 8 at Anaheim (which is located between Long Beach and Riverside). By the time that the air parcel defined at Long Beach at 1100 hours on August 31 reaches Rubidoux between 1600 and 1800 hours, a tremendous increase in NH_3 in the air parcel has occurred

(Figure 9b), and most of the inorganic nitrate again is found in the aerosol phase (Figure 9a). This increase in NH_3 is consistent with estimates of the spatial distribution of NH_3 sources in the Los Angeles area given by Cass et al. (1982) and Russell et al. (1983), which shows that the largest source of NH_3 in the Los Angeles area arises from a large group of dairies and animal husbandry operations in the Chino area just to the west of Riverside and Rubidoux.

The product of the measured concentrations of ammonia and nitric acid vapor is a key parameter that can be compared to the predictions of theoretical models for the ammonia and nitric acid concentrations expected at thermodynamic equilibrium with the aerosol phase. Nitric acid and ammonia concentration measurements were used to calculate their concentration product (CP) at each monitoring site. As seen in Figure 10, the measured CP at Rubidoux varies from less than 20 to over 300 ppbv^2 , and measured CP's at some monitoring sites were observed below 1 ppbv^2 . A very wide range of NH_3 and HNO_3 concentration product data thus have been acquired for use in verifying theoretical calculations. The hypothesis that aerosol nitrates were in equilibrium with gas phase nitric acid and ammonia during this experiment has been tested by Hildemann et al. (1984).

At two locations, Riverside and Pasadena, the major gaseous and aerosol species that evolve from NO_x emissions were measured. Figure 11 shows that most of the pollutant oxides of nitrogen at these two sites were present as NO and NO_2 throughout this experiment. Only a small fractional conversion of NO emissions to HNO_3 and NH_4NO_3 is

needed to explain the nitrate concentrations observed. The fractional conversion of NO and NO₂ to nitrate species during this experiment is lower than observed during some other field measurement programs (Grosjean, 1983; Spicer, 1982) but this is consistent with the lower level of photochemical activity experienced during this 2-day experiment. On the days sampled, peak 1-hr average O₃ concentrations exceeded 0.20 ppm at only a few monitoring sites, with the basin-wide 1-hr O₃ peak within the region shown in Figure 1 amounting to 0.26 ppm. In contrast, the O₃ concentration on the 1974 day modeled previously by Russell et al. (1983) exceeded 0.40 ppm with a correspondingly higher conversion of NO_x to HNO₃ and PAN.

4.0 Conclusion

Results from the field experiment show that the ionic material in the aerosol phase throughout the South Coast Air Basin is chemically complex. At most times, the bulk of the ionic aerosol is composed of nitrate, sulfate and ammonium ion. However there are significant amounts of Na⁺, Ca⁺⁺, Mg⁺⁺, K⁺, Cl⁻ and possibly CO₃⁼, OH⁻ or H⁺ ions also present. The coastal nitrate-containing aerosol has a significant sea salt derived fraction, probably from the displacement of chloride by reaction with nitric acid. These multi-component aerosols are more complex than can be handled by present mathematical models for the equilibrium between HNO₃, NH₃ and a mixed sulfate, nitrate and ammonium containing aerosol.

Trajectory analysis has been used to judge the importance of transport in determining aerosol nitrate concentrations. Large amounts of nitrate were shown to accumulate in an air mass that stagnated near the coast at night. Later, this nitrate laden air mass was transported inland by the sea breeze. The time of the nitrate peak inland near Riverside coincided with the time that that nitrate laden air mass reached that area. This indicates that a description of transport characteristics as well as atmospheric chemistry is important in understanding the dynamics that govern the high nitrate levels observed in the eastern portion of the Los Angeles basin.

A nitrogen balance constructed at two locations in the Los Angeles basin shows that conversion of only a small fraction of the NO_x emissions to HNO_3 and NH_4NO_3 is sufficient to explain the aerosol nitrate and nitric acid observed. The two days studied here were both considered to have moderate smog (fairly typical of a summer day), and a correspondingly lower oxidation of NO_x to HNO_3 and PAN than would occur during an extreme air pollution episode in Los Angeles.

The data set derived from this experiment can be used in verification tests of aerosol nitrate formation models, and will challenge the predictive capability of current air quality models. The days sampled during this experiment exhibited both interesting transport patterns and evidence of chemical transformations that can be used to test both the transport and gas-to-particle conversion descriptions built into regional scale air quality models.

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TABLE 1
Measurement Uncertainties

| SPECIES | UNCERTAINTY DUE TO CHEMICAL ANALYSIS PROCEDURE* | UNCERTAINTY DUE TO FILTER BLANK [†] |
|-------------------|---|---|
| NO_3^- | 15% | $1.0 \mu\text{g m}^{-3}$ |
| $\text{SO}_4^{=}$ | 15% | $1.6 \mu\text{g m}^{-3}$ |
| Cl^- | 22% | $0.6 \mu\text{g m}^{-3}$ |
| NH_4^+ | 20% | $0.2 \mu\text{g m}^{-3}$ |
| Ca^{++} | 18% | $1.4 \mu\text{g m}^{-3}$ |
| Na^+ | 15% | $0.8 \mu\text{g m}^{-3}$ |
| K^+ | 18% | $1.1 \mu\text{g m}^{-3}$ |
| Mg^{++} | 18% | $0.5 \mu\text{g m}^{-3}$ |
| HNO_3 | 15% | $0.8 \mu\text{g m}^{-3}$ |
| NH_3 | 20% | $0.3 \mu\text{g m}^{-3}$ |

* One standard error, as % of nominally measured value

[†] One standard error, stated in equivalent atmospheric concentration

FIGURE CAPTIONS

- Figure 1. Locations of Nitrate Monitoring Sites in the South Coast Air Basin
- Figure 2. Schematic of the Sampling Apparatus Used at Nine of the Ten Sites. The tenth station used only the two 10 lpm lines with dual filters.
- Figure 3. a) Nitrate Concentrations Observed at Rubidoux, August 30-31, 1982.
b) Trajectory of the Air Mass Passing over the Long Beach Area at 1100 hours on August 31 and over the Rubidoux Area at 1800 hours on August 31, 1982.
c) Nitrate Concentrations at Long Beach, August 30-31, 1982.
- Figure 4. Ionic Species Concentration at Long Beach
a) Cations
b) Anions
- Figure 5. Ionic Species Concentration at Riverside
a) Cations
b) Anions
- Figure 6. Particulate Nitrate and Gaseous Nitric Acid Concentrations ($\mu\text{g m}^{-3}$ as NO_3^-)
a) Long Beach
b) Lennox
- Figure 7. Particulate Ammonium and Gaseous Ammonia Concentrations ($\mu\text{g m}^{-3}$ as NH_4^+)
a) Long Beach
b) Lennox
- Figure 8. a) Particulate Nitrate and Gaseous Nitric Acid Concentrations at Anaheim ($\mu\text{g m}^{-3}$ as NO_3^-)
b) Particulate Ammonium and Gaseous Ammonia Concentrations at Anaheim ($\mu\text{g m}^{-3}$ as NH_4^+)
- Figure 9. a) Particulate Nitrate and Gaseous Nitric Acid at Rubidoux ($\mu\text{g m}^{-3}$ as NO_3^-)
b) Particulate Ammonium and Gaseous Ammonia Concentrations at Rubidoux ($\mu\text{g m}^{-3}$ as NH_4^+)
- Figure 10. Partial Pressure Concentration Product of Ammonia and Nitric Acid at Rubidoux.
- Figure 11. Measured NO , NO_2 , HNO_3 , PAN and Nitrate (in $\mu\text{g m}^{-3}$ stated as equivalent NO_3^-)
a) Pasadena
b) Rubidoux

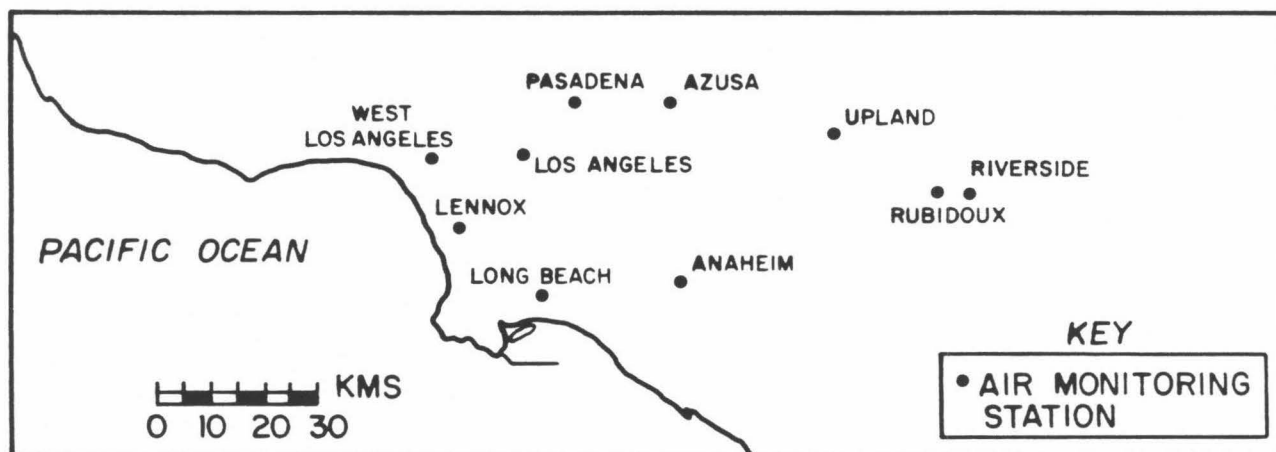
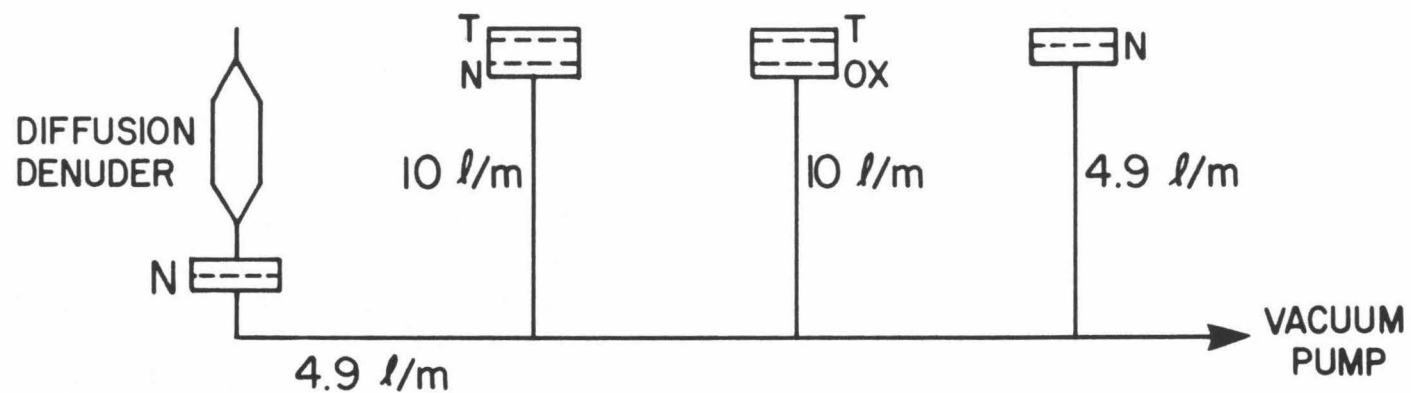
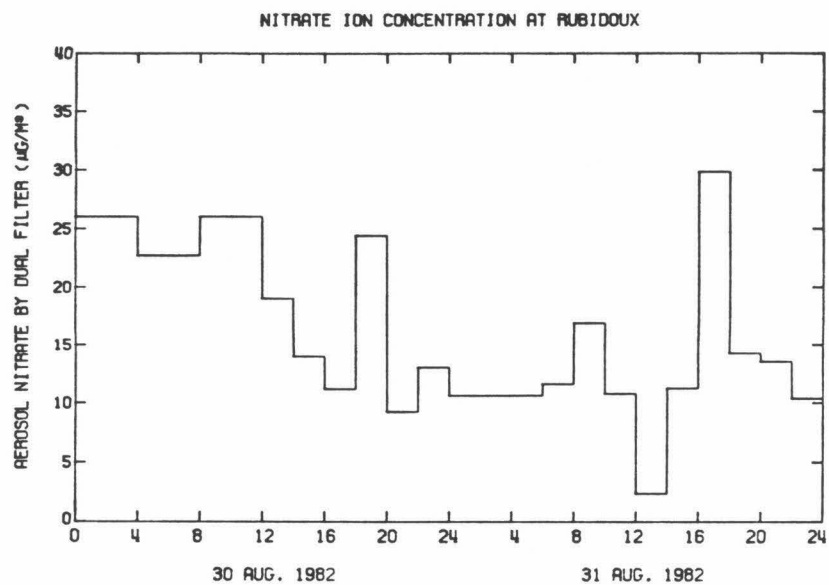


FIGURE 1

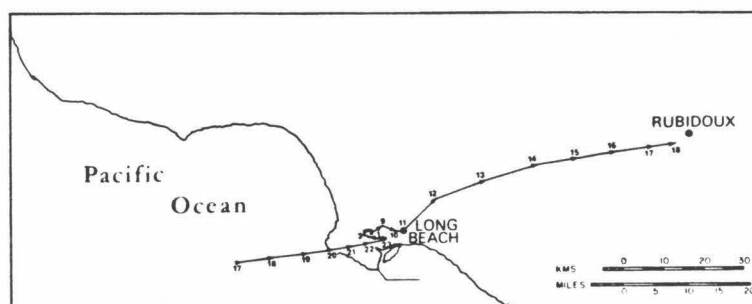


T - TEFLON FILTER
N - NYLON FILTER
OX - OXALIC ACID IMPREGNATED FILTER

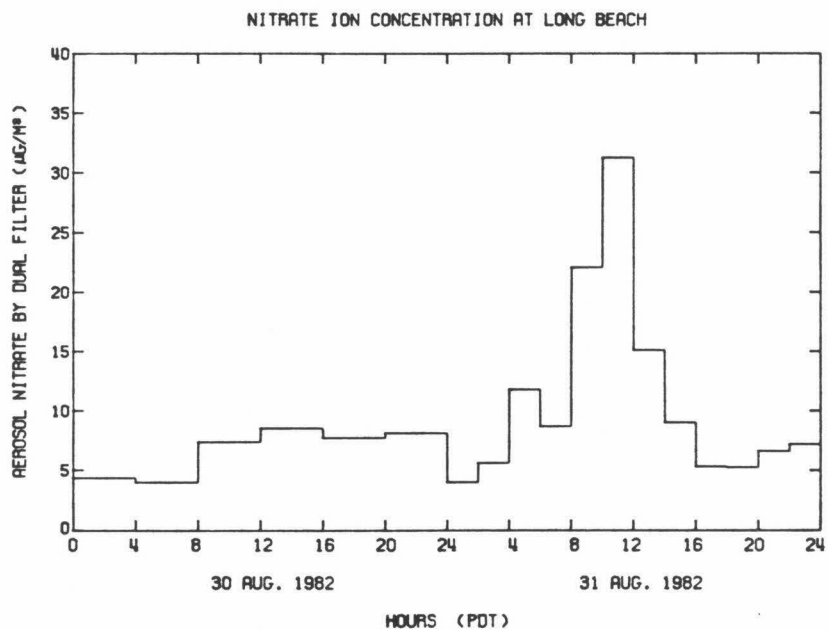
FIGURE 2



(a)

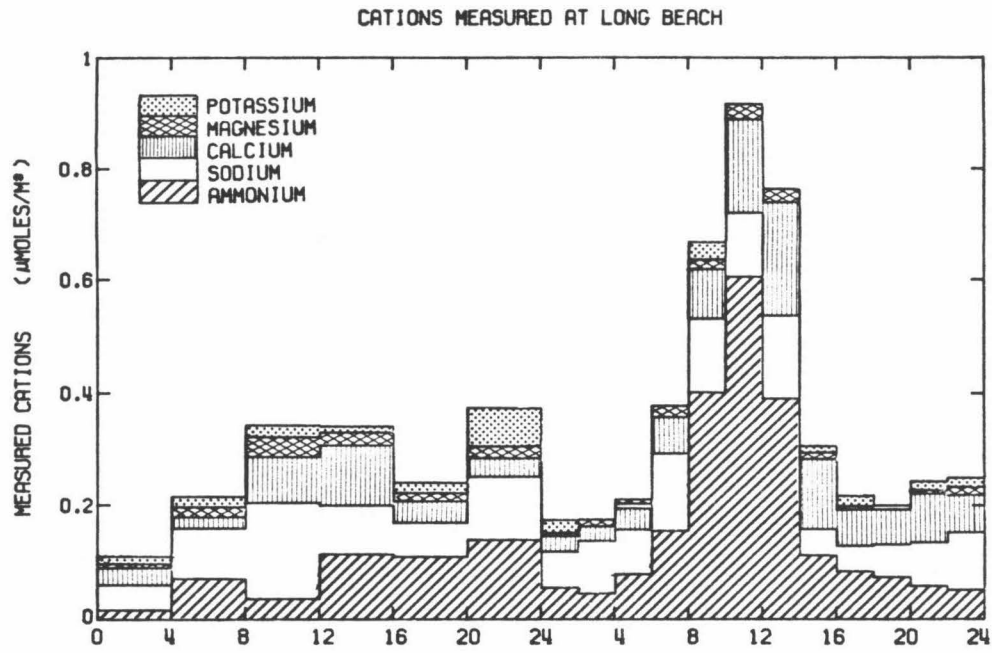


(b)

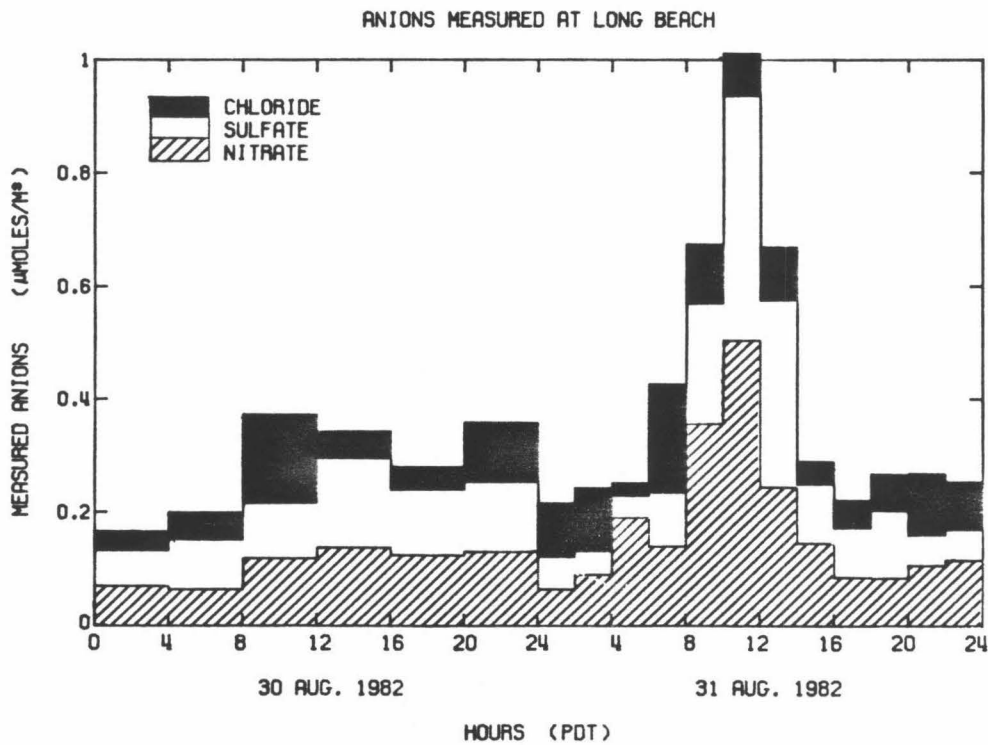


(c)

FIGURE 3



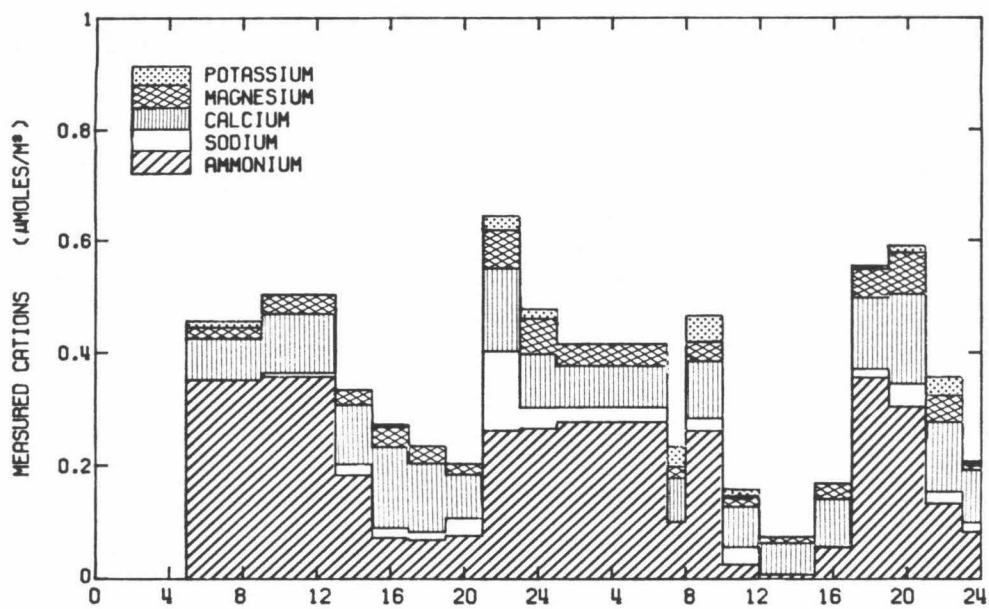
(a)



(b)

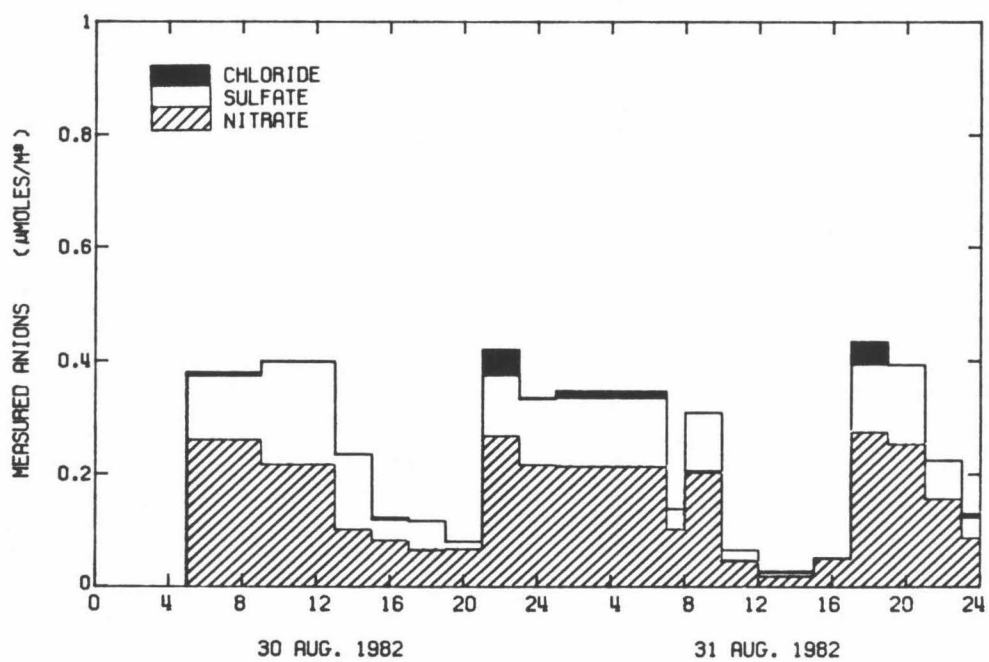
FIGURE 4

CATIONS MEASURED AT RIVERSIDE



(a)

ANIONS MEASURED AT RIVERSIDE

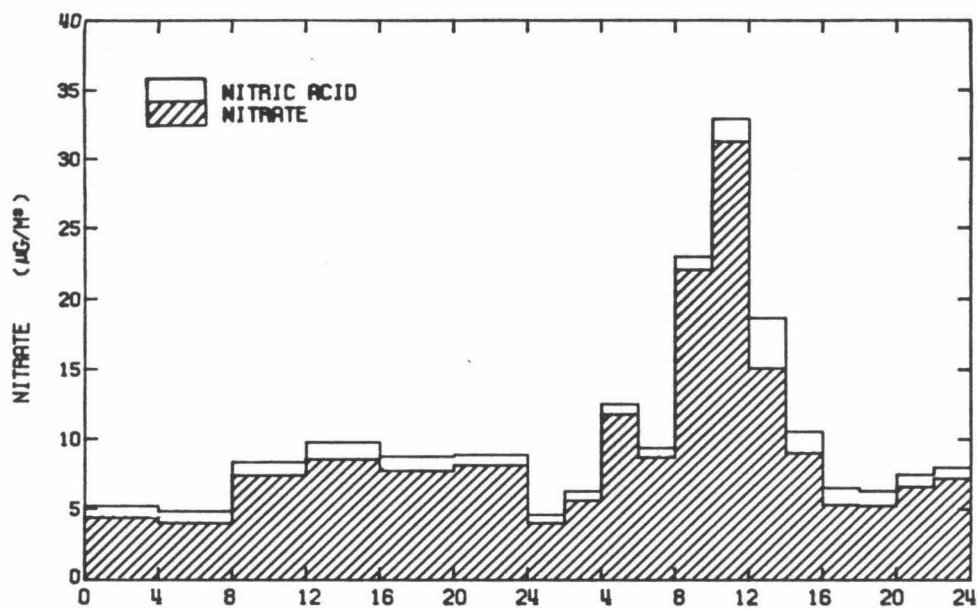


HOURS (PDT)

(b)

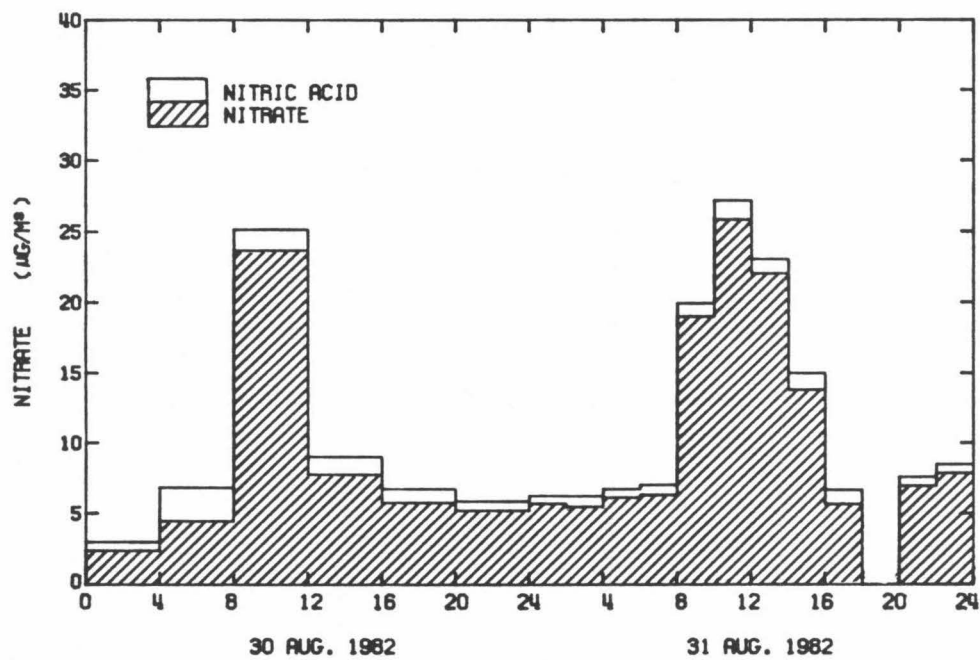
FIGURE 5

AEROSOL NITRATE AND NITRIC ACID VAPOR AT LONG BEACH



(a)

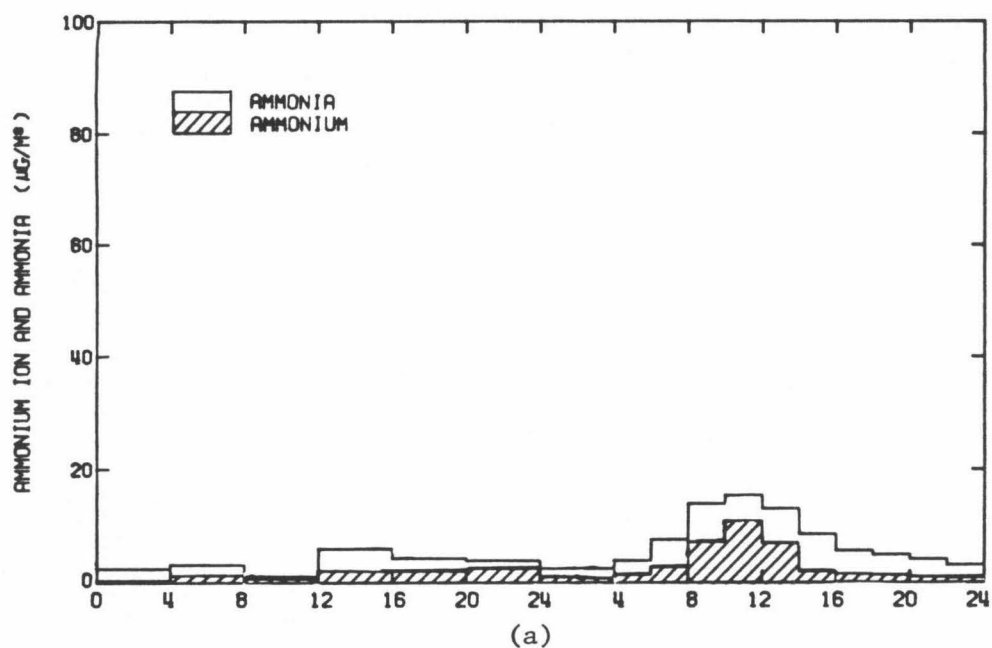
AEROSOL NITRATE AND NITRIC ACID VAPOR AT LENNOX



HOURS (PDT)
(b)

FIGURE 6

AMMONIUM ION AND AMMONIA AT LONG BEACH



AMMONIUM ION AND AMMONIA AT LENNOX

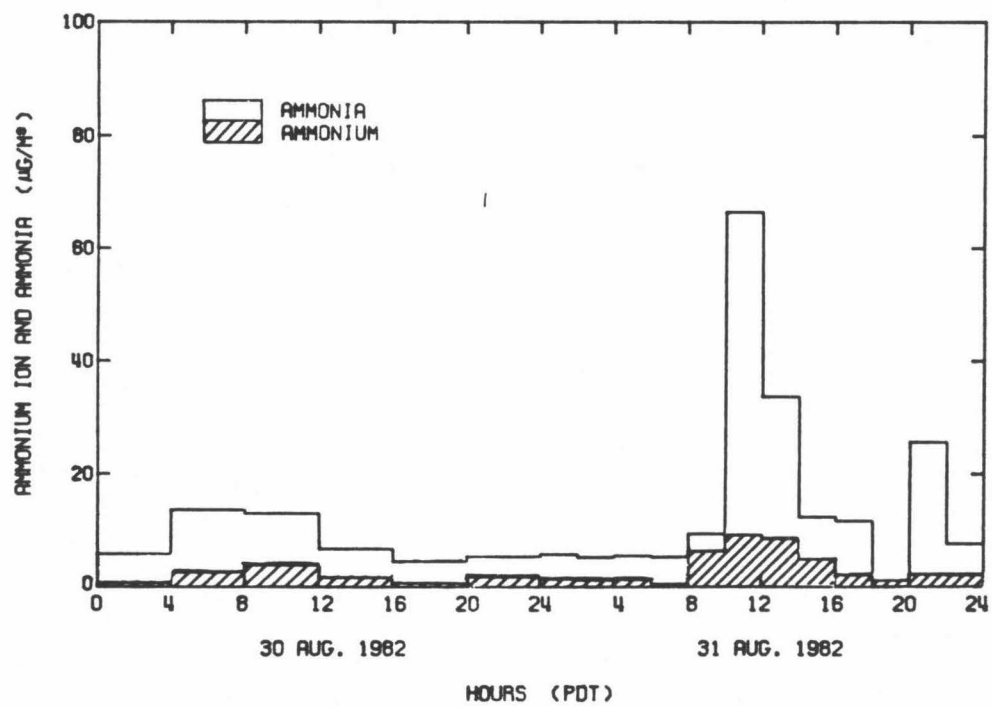
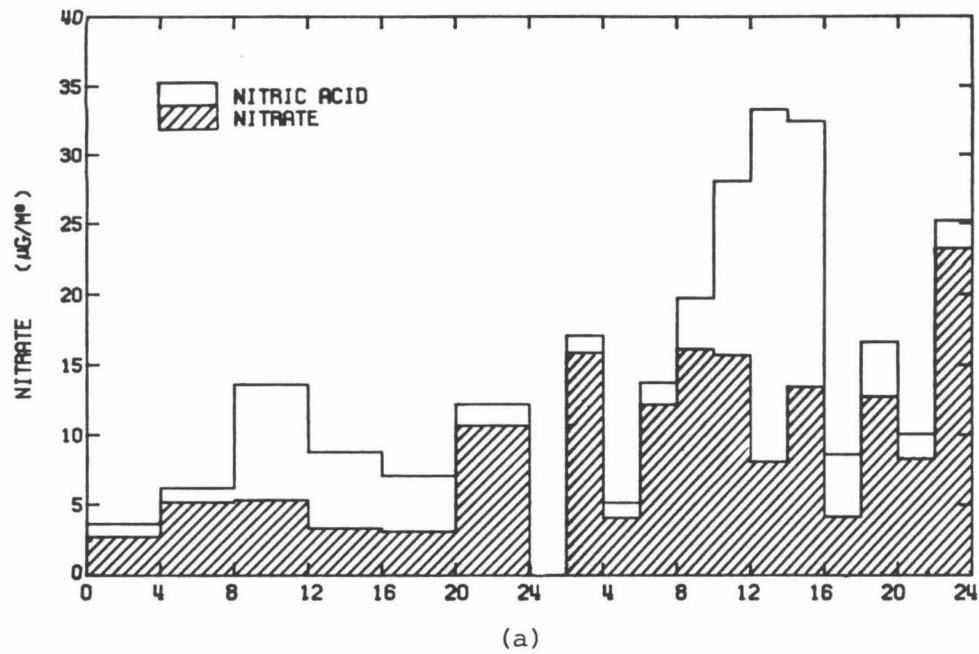


FIGURE 7

AEROSOL NITRATE AND NITRIC ACID VAPOR AT ANAHEIM



AMMONIUM ION AND AMMONIA AT ANAHEIM

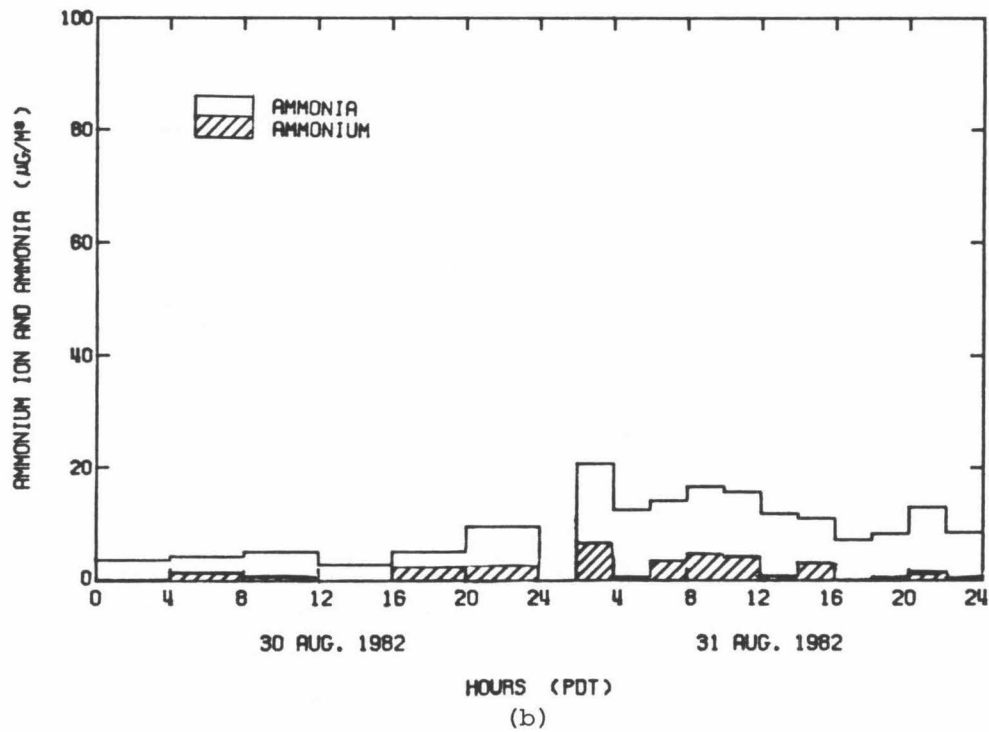
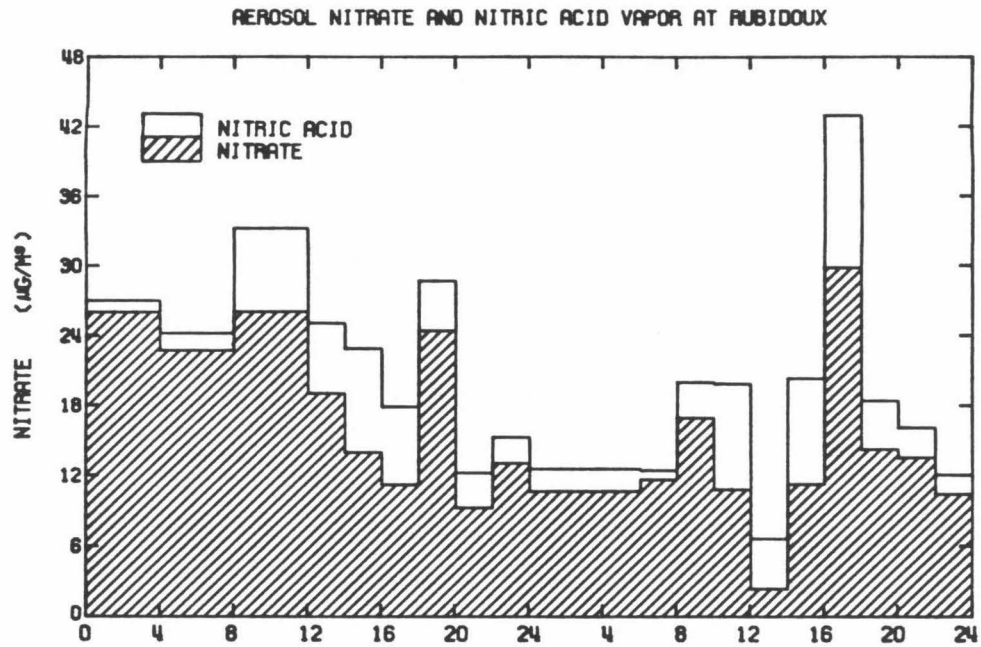
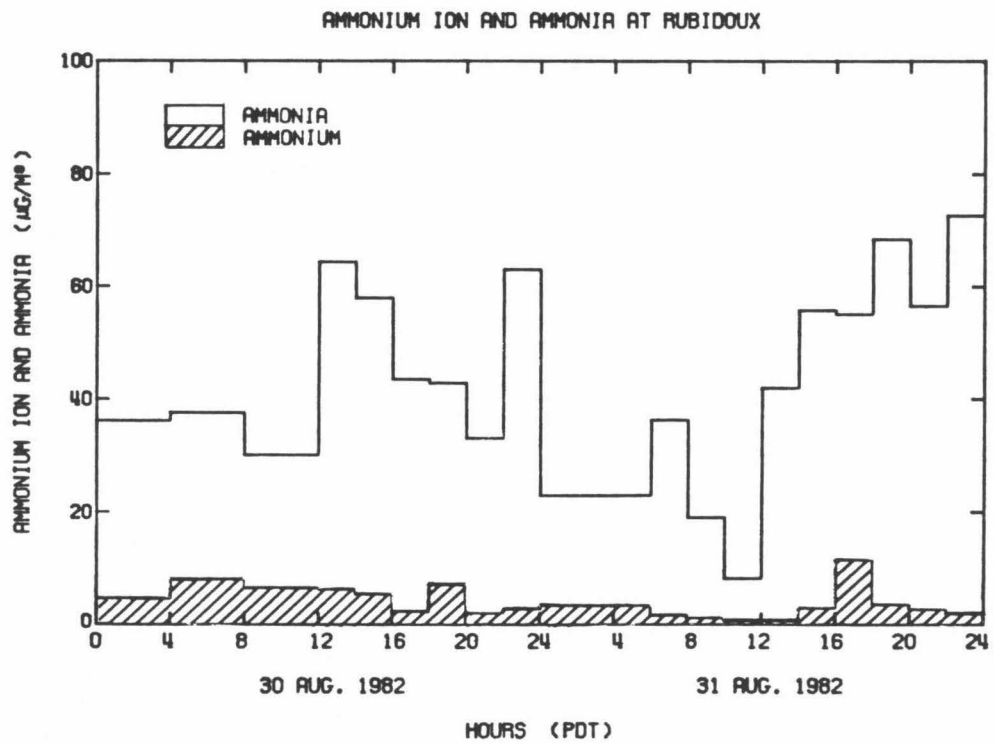


FIGURE 8



(a)



(b)

FIGURE 9

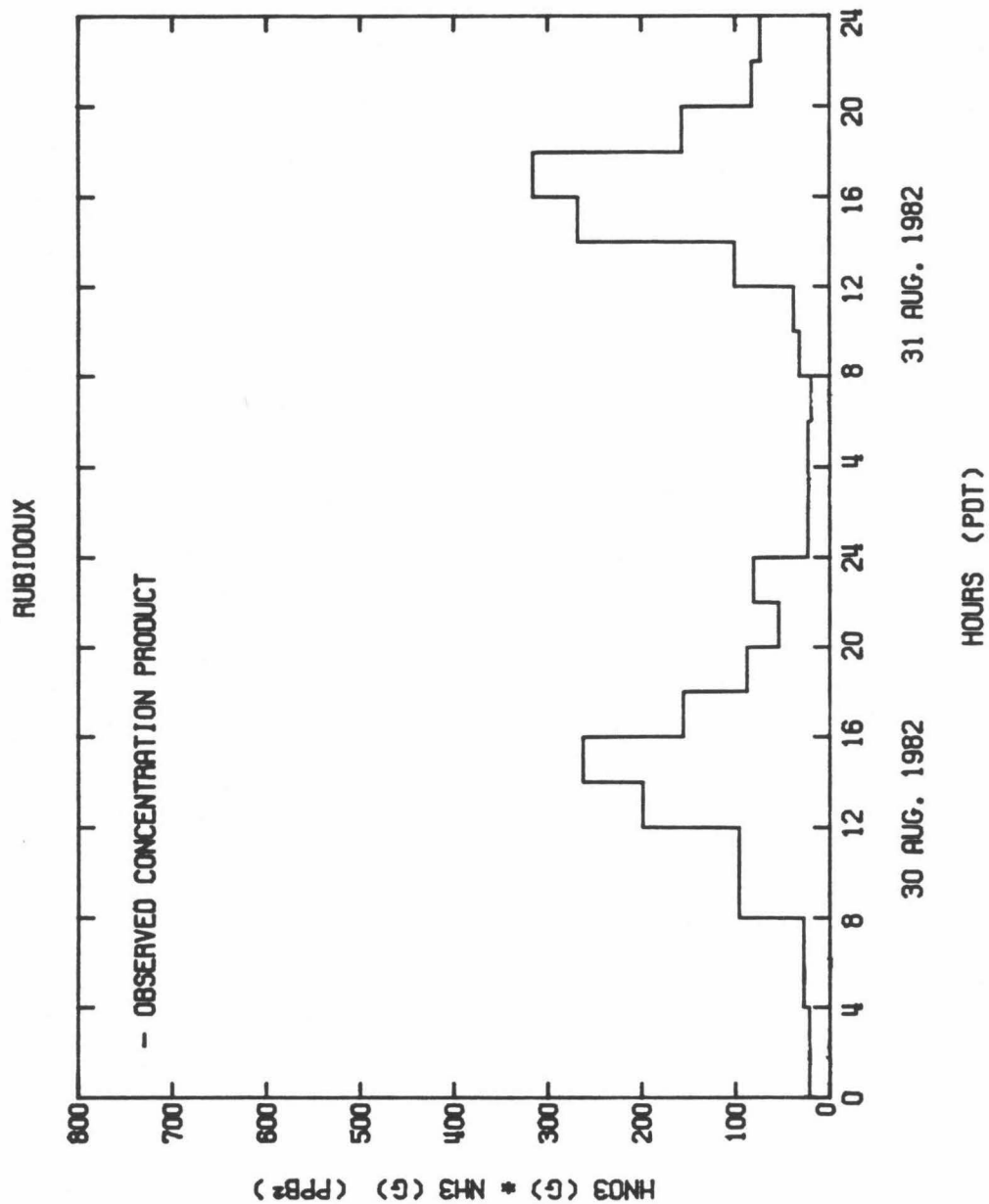


FIGURE 10

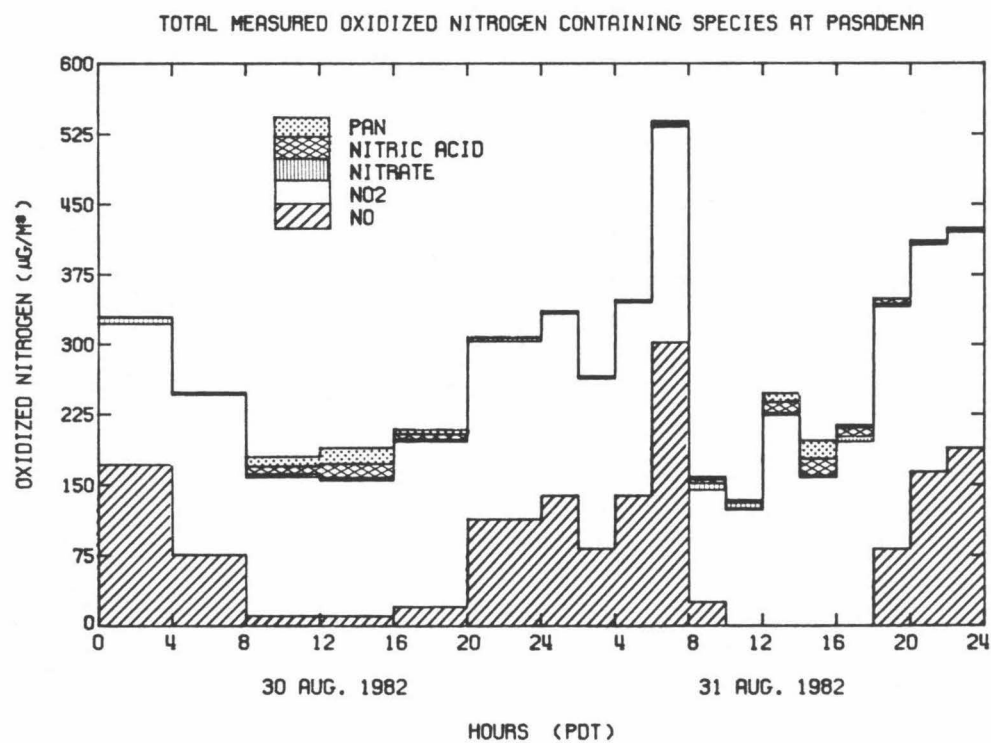
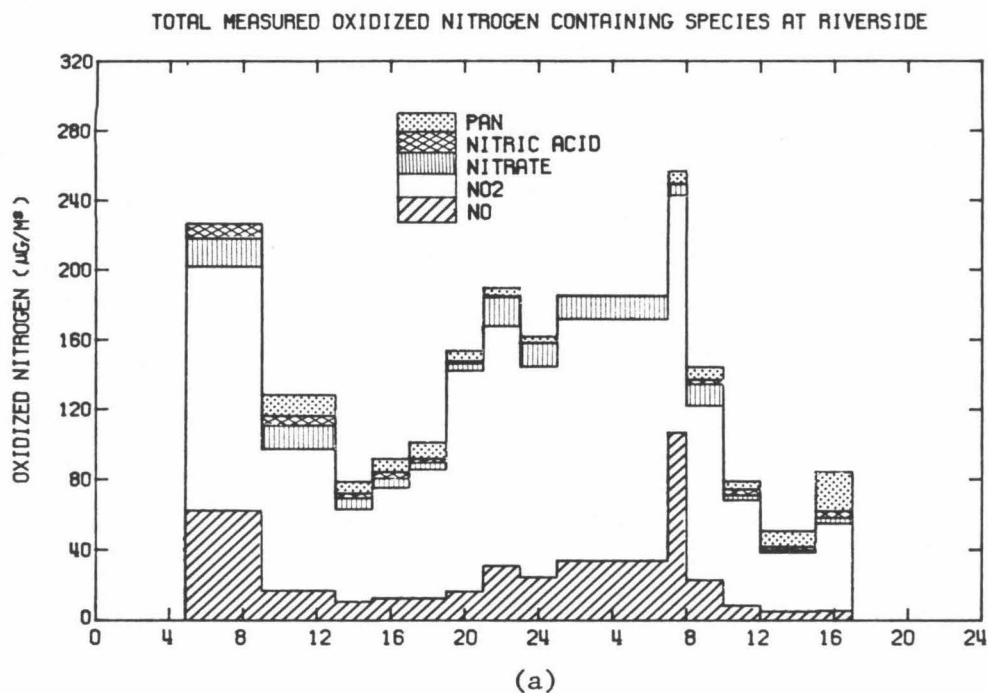


FIGURE 11